Electric field shielding in dielectric nanosolutions

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Abstract

To gain some insight into electrochemical activity of dielectric colloids of technical and biomedical interest we investigate a model of dielectric nanosolution whose micro-constitution is dominated by dipolarions – positively and negatively charged spherically symmetric nano-structures composed of ionic charge surrounded by cloud of radially polarized dipoles of electrically neutral molecules of solvent. Combing the standard constitutive equations of an isotropic dielectric liquid with Maxwell equation of electrostatics and presuming the Boltzmann shape of the particle density of bound-charge we derive equation for the in-medium electrostatic field. Particular attention is given to numerical analysis of obtained analytic solutions of this equation describing the exterior fields of dipolarions with dipolar atmospheres of solvent molecules endowed with either permanent or field-induced dipole moments radially polarized by central symmetric field of counterions. The presented computations show that the electric field shielding of dipolarions in dielectric nanosolutions is quite different from that of counterionic nano-complexes of Debye-Hückel theory of electrolytes.

Keywords: dielectric nanosolutions, in-medium dipolarions, electric field shielding

1 Introduction

There is a common recognition today that electrochemical activity of a wide class of non-magnetic colloids of technical and biomedical interest is primarily determined by the electrostatics of internal nano-structures of an extremely involved molecular composition. This complexity calls for the development of admittedly idealized models of such nano-complexes providing a comprehensive insight into in-medium electrostatics of both conducting and

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dielectric nanosolutions. A well-known example is the macroscopic treatment of spherical nano-structures in globular polyelectrolytic biosolutions borrowing the idea of quasi-particles from the Debye-Hückel (DH) theory of weak electrolytes. As is known, the standard DH-theory (and set of its modifications, e.g. [1,2]) deals with completely ionized (highly conducting) solutions in which the ions are regarded as non-polarized free spherical charges. The basic explanatory device of DH-theory is the in-medium quasiparticle composed of a massive macro-ion surrounded by an atmosphere of light counterions. The central to this theory is the approximation of particle density in ionic atmosphere by Boltzmann function with the energy factor depending on the potential of mean electrostatic field. The most striking outcome the DH-approach to electrostatics of electrolytes, relying on the linearized Poisson-Boltzmann equation for the potential of exterior Coulomb (electrostatic) field of above quasiparticles, is that the solution of this latter equation provides proper account for the in-medium effect of electric field shielding [2].

On the other hand, the situation is not so clear for nanosolutions possessing properties of dielectric (non-conducting) liquids the sources of internal electric field in which are bound charges rather than free ones as is the case of electrolytes. The electrodynamics of continuous dielectric media teaches us that the local density of bound charges ρ_b owe its origin to gradients of dielectric permittivity ϵ in the direction of local electric field $\mathbf{E}$, but the interrelation between this field and micro-composition of dielectric media remains less studied. In this paper we investigate this issue in the model of dielectric nanosolution whose micro-composition is dominated by spherically symmetric nano-complexes composed of massive counterions coagulated by cloud of polarized dipoles of solvent molecules. In what follows such nano-structures are dubbed by *dipolarions*. In so doing we focus on computing exterior fields for two kinds of such nano- complexes, namely (i) permanent dipolarion composed of macro-ion coated by atmosphere of polarized dipoles of polar molecules with constant (field-independent) intrinsic dipole moments, and (ii) field-induced dipolarion the atmosphere of which consists of molecules whose dipole moments are induced by field of macro-ion. Before embarking on mathematical details of in-medium electrostatics of such nanosolution, it seems worth emphasizing that dipolarion is the electrically charged nano-complex, as is illustrated in Fig. 1 showing internal constitution of permanent dipolarions with a positive and a negative charges of central macro-ions. The effect of polarization of solvent molecules along the lines of central symmetric field of micro-ion consists in an effective shift of charge from center to the surface of the dipolarion with no change of the original sign of charge of micro-ion. Thus, the physical nature of electric field shielding in dielectric nanosolutions with the above dipolarion micro-constitution is substantially different from that for DH-quasiparticles of electrolytes. This observation motivates the main purpose of this work which is to compute to exterior electric fields of dipolarions in dielectric nanosolution carry-

ing information about the in-medium effect of electric field shielding. In the below presented calculations this effect is highlighted by difference between obtained analytic expressions for exterior fields of dipolarions and canonical formula for Coulomb field of charged sphere immersed in a dielctric liquid composed of electrically passive, unpolarizable, molecules.

2 Basic equations of in-medium electrostatics of dipo-larion nanosolution

The electrostatic state of an isotropic dielectric continuous medium is described by equations (e.g., [3])

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}, \quad \nabla \cdot \mathbf{E} = \rho \tag{1}$$

where $\mathbf{D}$ is the field of electric displacement, $\mathbf{P}$ is the density of electric polarization - electric dipole moment per unit volume and ϵ_0 stands for the electric permittivity of free space. The rightmost of (1) is the Maxwell equation for the electrostatic field $\mathbf{E}$ (differential form of Coulomb law) and ρ is the total density of electric charge which is a sum of the free charge density, ρ_f, and bound charge density, ρ_b. By definition these are

$$\rho = \rho_f + \rho_b, \quad \nabla \cdot \mathbf{D} = \rho_f, \quad \nabla \cdot \mathbf{P} = -\rho_b. \tag{2}$$

As was mentioned, the main difference between dielectric liquids and electrolytes is that the former can be usually thought of as a non-conducting suspension composed of bound charges dissolved in a fluid matrix of electrically polarized molecules, whereas electrolyte is an electrically conducting solution (of second type) whose conductivity is attributed to the mobility of ions which are regarded as free (non-bounded) charges. Taking this into account and putting $\nabla \cdot \mathbf{D} = \rho_f = 0$, one has

$$\nabla \cdot (\epsilon_0 \mathbf{E}) = \rho_b \tag{3}$$

Here $\mathbf{E}$ stands for the internal electric mean field whose source is the bound-charge density charges which is formed from charges of both counterions and poles of molecular dipoles. In this work, as was stated, we focus on a dielectric nanosolution whose internal electrification is determined by dipolarions - nano-structures composed of monopole charge of counterions surrounded by a cloud of radially polarized molecular dipoles forming dipolar atmospheres, having some features in common with ionic atmosphere of DH-qiasiparticle. Bearing this mind we represent the macroscopic bound-charge density of dielectric nanosolution in the form $\rho_b = q_i \tilde{n}_i / \epsilon$ where index i labels counterions carrying the charge $q_i = e z_i$ and $\tilde{n}_i$ is the effective particle density of bound charges associated with the ion of i-th type which

takes into account polarization of molecular dipoles by field of given ion. The contribution of bound-charges of dipole-polarized molecules to the macroscopic bound-charge density of nanosolution can be incorporated in the above parametrization of ρ_b by using of Boltzmann function for $\tilde{n}_i$ with the energy factor describing polarization effect of ionic fields on dipole moment of molecules of solvent. Namely,

$$\rho_b = \frac{q_i \tilde{n}_i}{\epsilon}, \quad \tilde{n}_i = n_i\, e^{-\dfrac{N_\ell \mathbf{p}_\ell \cdot \mathbf{E}}{k_B T}} \tag{4}$$

where ϵ is electric permittivity of solvent, N_ℓ is the number of dipole-polarized molecules of ℓ-type having a dipole moment $\mathbf{p}_\ell$, which form the dipolar atmosphere surrounding the ion. In the last equation, by n_i is understood the effective particle density of ions in the the absence of dipolar polarization of solvent molecules, as it would be the case of dielectric liquid composed of ions dissolved in fluid matrix of electrically passive, unpolarizable, molecules (i.e., molecules which are non-polar and insensitive to fields of ions). Equation (4) means, in fact, that dipolar atmospheres of counterions are in thermal equilibrium at a temperature T which is high enough to approximate the average particle density of bound charges of dielectric solution in above fashion. With account of this we arrive at a highly non-linear equation of in-medium electrostatics

$$\nabla \cdot \mathbf{E} = \frac{\rho_0}{\epsilon_0 \epsilon}\, e^{-\dfrac{N_\ell \mathbf{p}_\ell \cdot \mathbf{E}}{k_B T}} \tag{5}$$

describing electric field in dielectric nanosolution with account its dipolarion micro-composition. In this equation by ρ_0 is understood the bound-charged density which would be in case of ions suspended in the solvent of unpolarizable molecules. Adhering to the spirit of Debye-Hückel theory, we make the following approximation

$$e^{-\dfrac{N_\ell \mathbf{p}_\ell \cdot \mathbf{E}}{k_B T}} \approx 1 - \frac{N_\ell}{k_B T}\, \mathbf{p}_\ell \cdot \mathbf{E}.$$

As a result, the equation of in-medium electrostatics of dipolarionic nanosolution takes the form

$$\nabla \cdot \mathbf{E} + \frac{q_i n_i}{\epsilon_0 \epsilon} \frac{N_\ell}{k_B T}\, \mathbf{p}_\ell \cdot \mathbf{E} = \frac{q_i n_i}{\epsilon_0 \epsilon}. \tag{6}$$

This equation constitutes mathematical basis for below presented analysis of the electric field shielding in the dielectric nanosolution with the dipolarion micro-constitution.

3   In-medium shielding of dipolarionic electric fields

In the reminder, we focus on application of the equation (6) to electrostatics of in-medium dipolarions having a shape of sphere of radius R In accord with the standard approach to

the problem of electrostatic field inside and outside sphere, the interior, $\mathbf{E}_i = E(r < R)$, and exterior, $\mathbf{E}_e = E(r > R)$, fields should be computed from two equations

$$\nabla \cdot \mathbf{E}_i + \eta_\ell \, \mathbf{p}_\ell \cdot \mathbf{E}_i = \frac{q_i n_i}{\epsilon_0 \epsilon}, \quad r \leq R, \qquad \eta_\ell = \frac{q_i n_i}{\epsilon_0 \epsilon} \frac{N_\ell}{k_B T}, \tag{7}$$

$$\nabla \cdot \mathbf{E}_e + \eta_\ell \, \mathbf{p}_\ell \cdot \mathbf{E}_e = 0, \quad r > R. \tag{8}$$

supplemented by boundary conditions on the surface of dipolarion of radius R. In the above equations η_ℓ is the in-medium parameter which accounts for the dipole polarization of solvent molecules from dipolar atmosphere by field of monopole charge of central micro-ion. As was noted in introduction, we are considering the two kinds of dipolarions distinguishing by type of solvent molecules forming its dipolar atmosphere. The first model belongs to aqua and aqua-like solutions composed of polar molecules of solvent, that is, molecules endowed with permanent dipole moments of constant magnitude, $\mathbf{p}_\ell = $ constant. The nano-complex of this type is referred to as a permanent dipolarion. The second model belongs to a case of dipolar atmosphere consisting of N_ℓ non-polar molecules whose dipole electric moments $\mathbf{p}_\ell$ are induced by local fields $\mathbf{E}$ of macro-ions: $\mathbf{p}_\ell = \alpha_\ell \, \mathbf{E}$, where constant parameter α_ℓ is the molecular polarizability of solvent molecule of ℓ-sort. The in-medium dipolarion of this type is referred to as a field-induced dipolarion. Since our prime goal is the in-medium effect of electric field shielding, in what follows we focus on exterior fields of above dipolarions whose central symmetric shape suggests that the local fields have only one radial component

$$\mathbf{E}(r) = -\nabla \Phi(r), \quad [E_r(r) = -\nabla_r \Phi(r), \ E_\theta = 0, \ E_\phi = 0]. \tag{9}$$

3.1   Exterior field of permanent dipolarion

Taking into account the last remark presuming that $N_\ell \mathbf{p}_\ell \cdot \mathbf{E}_e = N_\ell \, p_\ell \, E_e$, one finds that the radial component of exterior field of permanent dipolarion obey the liner equation

$$\nabla_r E_e(r) + \lambda^{-1} \, E_e(r) = 0, \quad r > R, \quad \lambda^{-1} = \frac{q_i \, n_i}{\epsilon_0 \epsilon} \frac{N_\ell \, p_\ell}{k_B T}. \tag{10}$$

With the help of substitution $E_e(r) = u(r)/r^2$ we arrive at equation for $u(r)$ permitting the general solution

$$\frac{du}{dr} + \lambda^{-1} \, u = 0 \quad \rightarrow \quad u = u_0 \, e^{-r/\lambda}. \tag{11}$$

As a result, for the radial component of external electrostatic field of permanent dipolarion we obtain

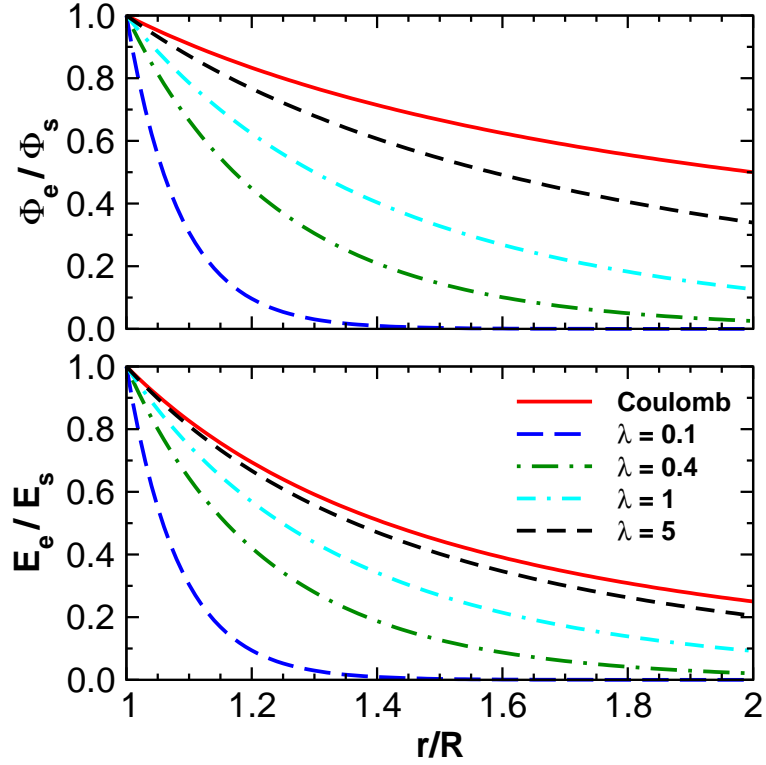$$E_e(r) = \frac{q}{4\pi\epsilon_0\epsilon} \frac{e^{-r/\lambda}}{r^2} \tag{12}$$

Figure 1: Normalized to their surface values the external potential Φ_e/Φ_s and the radial component of external field E_e/E_s of permanent dipolarion computed as functions of r/R with pointed out values of parameter of length λ regulating the spatial character of the exterior electric field shielding. A case $\lambda = 0$ corresponds to the exterior field of uniformly charged sphere in dielectric liquid composed of electrically passive molecules, insensitive to dipolar polarization.

where q is the total charge of dipolarion whose density accounts for the internal polarization of polar molecules by fields of central ion. The potential of this field is given by equations

$$\frac{d\Phi_e}{dr} = -\frac{q}{4\pi\epsilon_0\epsilon}\frac{e^{-r/\lambda}}{r^2}, \tag{13}$$

$$\Phi_e(r) = -\frac{q}{4\pi\epsilon_0\epsilon}\left[\frac{\text{Ei}(1, r/\lambda)}{\lambda} - \frac{e^{-r/\lambda}}{r}\right], \quad \text{Ei}(n, x) = \int\limits_1^\infty \frac{e^{-xt}}{t^n}\, dt. \tag{14}$$

where $\text{Ei}(1, r/\lambda)$ is the Exponential integral (e.g., [4]). Special comment should be made regarding the obtained expression (12) for electric field of dipolarion whose exponential factor exhibits the in-medium effect of electric field shielding. This effect is controlled by parameter λ depending on characteristics of both counterions and molecules of solvent: the larger λ the smaller effect of shielding. Also, it worth emphasizing that the magnitude of the shielding length λ is the in-medium parameter carrying information about all constituents of dielectric nanosolution, since depends upon bound-charged density of all counterions $q_i n_i$, electric permittivity ϵ and dipole moments of solvent molecules p_ℓ. The shielding of exterior field of permanent dipolarion is clearly demonstrated in Fig.1 where we plot exterior field and potential as functions of distance from the dipolarion surface (normalized to its radius) computed at pointed out values of the shielding length λ.

3.2   Exterior field of field-induced dipolarion

Consider a model of field-induced dipolarion which might be appropriate to dielectric nanosolutions composed of non-polar molecules of solvent which are easily polarized, however, by fields of counterions: under the action of ionic field the molecules of dipolar atmospheres acquire a dipole electric moments which are proportional to the field of ion: $\mathbf{p}_\ell = \alpha_\ell\,\mathbf{E}$, where ℓ labels the dipolar type of molecule. Interestingly enough that the exterior electrostatic field of field-induced dipolarion is described by non-linear equation

$$\nabla\cdot\mathbf{E}_e + \varkappa\,\mathbf{E}_e^2 = 0, \quad \mathbf{E}_e = -\nabla\Phi_e, \quad r > R \quad \varkappa = \frac{q_i n_i}{\epsilon_0\epsilon}\frac{N_\ell\,\alpha_\ell}{k_B T} \tag{15}$$

which can be solved analytically. However to avoid destructing attention to mathematical details of fairly tedious analytic computations (which will be reported in separable paper), we present here the final result

$$\mathbf{E}_e = \frac{q}{4\pi\epsilon_0\epsilon}\frac{1}{r(r - q\varkappa)}\,\mathbf{e}_r \tag{16}$$

which can easily be verified by simple computation

$$\nabla\cdot\mathbf{E}_e = \frac{1}{4\pi\epsilon_0\epsilon}\frac{-\varkappa q^2}{r^2(r - \varkappa q)^2}, \quad \varkappa\mathbf{E}_e^2 = \frac{1}{4\pi\epsilon_0\epsilon}\frac{\varkappa q^2}{r^2(r - \varkappa q)^2}. \tag{17}$$

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The exterior field and its potential can be represented in the form

$$\mathbf{E}_e = \frac{q}{4\pi\epsilon_0\epsilon\, r^2}\left(1 - \frac{\Lambda}{r}\right)^{-1}\mathbf{e}_r, \quad \Phi_e(r) = -\frac{q}{\Lambda}\ln\left(1 - \frac{\Lambda}{r}\right), \quad \Lambda = \frac{q_i n_i}{4\pi\epsilon\epsilon_0}\frac{N\alpha}{k_B T} \quad (18)$$

highlighting the effect of the field shielding which is regulated by parameter Λ depending upon charges of macro-ions and electric polarizability of solvent molecules. Here by q is understood the total charge of field-induced dipolarion.

It is seen that, unlike the exponential shielding of electric field of the permanent dipolarion, the dipolar atmosphere of field-induced dipolarion leads to the electric field shielding which is described by $(1 - \Lambda/r)$ factor. The above characteristics can be conveniently represented via dimensionless parameter of the field shielding λ and distance (normalized to the dipolarion radius) $x = r/R > 1$ which is measured from the surface of dipolarion

$$\lambda = \frac{\Lambda}{R}, \qquad 0 < \lambda < 1, \qquad x = \frac{r}{R} > 1. \qquad (19)$$

In terms of these quantities, the radial component of external field $\mathrm{E}_e(x)$ and potential $\Phi_e(x)$ take the form

$$\mathrm{E}_e(x) = \frac{q}{4\pi\epsilon_0\epsilon}\frac{1}{x^2\,R^2}\left(1 - \frac{\lambda}{x}\right)^{-1}, \qquad \Phi_e(x) = -\frac{q}{4\pi\epsilon_0\epsilon}\frac{1}{\lambda\,R}\ln\left(1 - \frac{\lambda}{x}\right). \qquad (20)$$

The case of $x = 1$ corresponds to the surface values of these quantities. In Fig.2, we plot the radial component of exterior electric field and potential of the field-induced dipolarion as functions of x computed at different values of parameter of shielding length λ. One sees, the smaller λ the less in-medium effect of the field shielding. The limiting case of $\lambda = 0$ corresponds to Coulomb law for the potential and field of uniformly charged sphere.

4   Summary

An understanding of macroscopic electrodynamics of non-conducting nanomaterials possessing dielectric and/or ferroelectric properties is important for their practical applications in current industrial and biomedical nanotechnologies. For example, in Ref. [5], an optical response of ferroelectric nanoparticles by resonant vibrations has been studied in the context of their potential utilization as biolabels. Continuing this line of research, the purpose of this work was to find out theoretical framework providing meaningful discussion of electrochemical properties of dielectric nanosolution originating from dipolarions – positively and negatively charged nano-complexes composed of counterions coagulated by clouds of electric dipoles of solvent molecules. Employing the standard equation of electrostatics for dielectric continuous media and using Boltzmann distribution for the particle density of bound charges, we found that in-medium electrostatics of such nanosolutions can be conveniently described
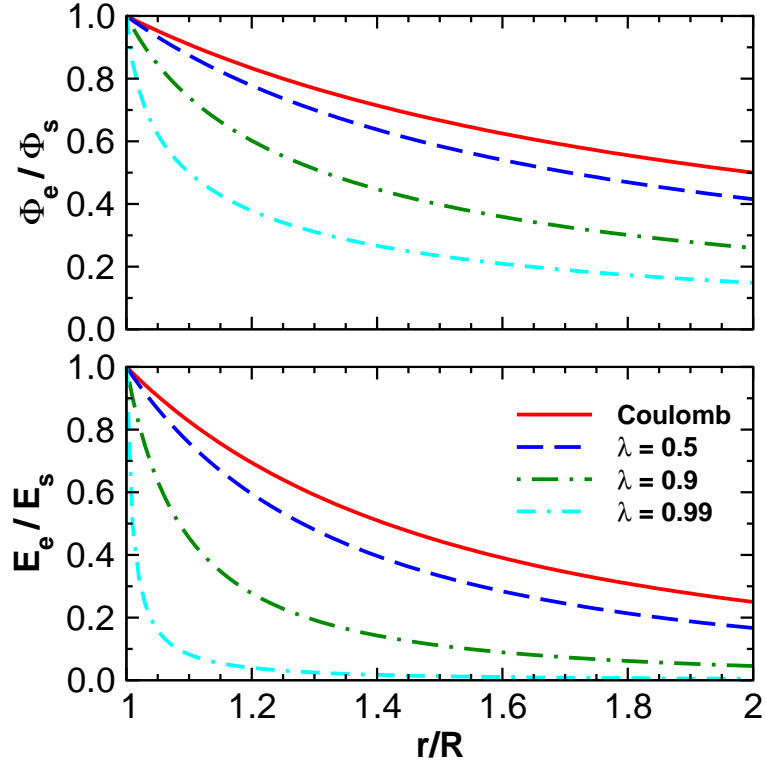
Figure 2: The potential Φ_e/Φ_s and field E_e/E_s (normalized to their magnitudes on the surface) as a function of $x = r/R$ from field-induced dipolarion computed for different values of parameter λ regulating intensity of electric field shielding.

by equation for the intensity of internal field, rather than rather Poisson-Boltzmann equation for electrostatic potential lying at the base of the Debye-Hückel theory of electrolytes. The introduced equations are interesting in their own right and, first of all, due to their capability of consistent mathematical description and physical treatment of the in-medium effect of electric field shielding which is caused by the polarization of molecular dipoles of solvent by fields of counterions. This capability has been demonstrated by numerical analysis of obtained analytic solutions for exterior fields of two kinds of dipolarions. From current investigations of technical and biolectrolytes we know that the electrostatic fields and potentials of in-medium quasiparticles serve as the basic ingredients in computations of coefficients of electrochemical activity of these conducting liquids. In the meantime, this issue has not, to the best of our knowledge, been properly discussed in the context of dielectric liquids and nanosolutions and will be the subject of our forthcoming paper relying on the results presented in this work.

Acknowledgements

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